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Baeumer, S. F. Bent

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Ultra-low loading Pt nanocatalysts prepared by atomic layer deposition on carbon aerogels

J. S. King¹, A. Wittstock^{2,3}, J. Biener², S. O. Kucheyev², Y. M. Wang², T. F. Baumann², S. Giri¹, A. V. Hamza², M. Baeumer³, and S. F. Bent¹

1. Department of Chemical Engineering, Stanford University, 381 North South Mall, Stanford, CA 94305, USA

2. Lawrence Livermore National Laboratory, Nanoscale Synthesis and Characterization Laboratory, 7000 East Avenue, Livermore, CA 94550, USA

3. Institut für Angewandte und Physikalische Chemie, Universität Bremen, Leobener Strasse NW2, 28359 Bremen, Germany

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Abstract

Using atomic layer deposition (ALD), we show that Pt nanoparticles can be deposited on the inner surfaces of carbon aerogels (CA). The resultant Pt-loaded materials exhibit high catalytic activity for the oxidation of CO even at loading levels as low as ~ 0.05 mg Pt/cm². We observe a conversion efficiency of nearly 100% in the temperatures range 150-250 °C, and the total conversion rate seems to be only limited by the thermal stability of our CA support in ambient oxygen. Our ALD approach described here is universal in nature, and can be applied to the design of new catalytic materials for a variety of applications, including fuel cells, hydrogen storage, pollution control, green chemistry, and liquid fuel production.

Body

Nanoparticle catalyst materials are an active area of research, with the potential for high impact in applications such as chemical manufacturing, pollution control, green chemistry, liquid fuel production, and power generation.¹⁻³ Particular emphasis has recently been placed on the

development of advanced catalysts and electrode materials for fuel cells through the incorporation of noble metal nanoparticles into high surface area carbon supports.⁴⁻⁶ The loading of catalyst particles into carbon nanostructures can be performed by a variety of methods, including the impregnation and reduction of metal salts into a support structure or the electrochemical deposition of catalyst particles on the carbon material. One of the challenges associated with the design of these electrode materials has been the development of methods that can reduce the overall loading of the costly noble metal catalyst while retaining the high catalytic activity of the material.⁷ For example, the economic viability of direct methanol fuel cells requires a reduction in Pt catalyst loading from current levels of 2 – 8 mg/cm² to below 1 mg/cm².⁵

Recently, atomic layer deposition (ALD) has been demonstrated to be an excellent method for uniformly coating the inner surfaces of porous nanostructures with a variety of materials.⁸⁻¹² Atomic layer deposition is a process that provides atomic layer control of thin film growth using sequential, self-limiting surface reactions.¹³ Since film growth is self-limiting for each deposition cycle, the ALD process can be used to deposit conformal films inside high aspect ratio structures. For example, ALD has been used to deposit both metals and metal oxides, such as ZnO, Al₂O₃, W, Cu, and Ru, inside nanoporous monoliths.⁸⁻¹¹ Our previous study⁹ has also revealed that ALD allows one to control the morphology of the deposited metal, discrete nanoparticles versus formation of a continuous film, through the surface chemistry. While the growth of nanoparticles is undesirable for many applications, this discovery suggests great promise in the field of catalysis where it allows one to maximize the accessible surface area of the catalyst. In addition, due to the self-limiting nature of the process, ALD can be used to

control the amount of catalyst deposited on the support material. Hence, the process is ideally suited to determine the lower limits of metal loading in a catalytically-active system.

Here, we use ALD to fabricate novel Pt-loaded catalysts derived from carbon aerogels (CAs). Such CAs are unique porous materials that exhibit numerous exceptional properties, including mechanical stability, continuous porosity, high surface area, and high electrical conductivity, and, as such, are attractive platforms for incorporation of catalytic particles. Using the ALD process, we show that Pt nanoparticles can be deposited on the inner surfaces of CA monoliths, and that the resultant Pt-loaded materials (Pt-CA), even those with extremely low areal densities of Pt ($\sim 0.047 \text{ mg/cm}^2$), exhibit high catalytic activities for the oxidation of carbon monoxide.

The CA support was synthesized using a procedure described elsewhere.¹⁴ The skeletal structure of the material consists of interconnected sub-micron-sized carbon ligaments that define a continuous macroporous network. Despite being macroporous, the CA support still exhibits appreciable surface area ($\sim 480 \text{ m}^2/\text{g}$) due to microporosity within the carbon ligaments. As-synthesized CA monoliths were mechanically thinned to form disks of approximately 1 cm diameter and 500 μm thickness.

Following a recipe from Ref. [15], we deposited Pt in CAs by ALD using the (methylcyclopentadienyl)-trimethylplatinum (MeCpPtMe_3 , Strem Chemical Co) / oxygen (dry air) ALD process in a warm wall reactor, with a wall temperature of 125 °C and a stage temperature of 320 °C. Since the Pt ALD temperature window is relatively narrow, it was important to ensure that the CA substrate was at the right temperature during deposition. To increase heat transfer from the stage to the CA, hot wall conditions were replicated by placing CA disks inside a machined Al container with a perforated lid. This container was then placed

inside the reactor directly on the heated stage. Due to the relatively low vapor pressure of MeCpPtMe_3 (~ 800 mTorr at 65°C)¹⁶ and a tortuous porosity of the CA support, very long pulse and purge times were used to maximize penetration of the ALD precursors into and removal of byproducts out of the CA support. A single ALD cycle consisted of a 20 minute MeCpPtMe_3 pulse followed by a 10 minute N_2 purge, a 10 minute dry air pulse, and a 10 minute N_2 purge. In order to maximize precursor usage, quasi-static conditions were used for the MeCpPtMe_3 pulses, during which the chamber, isolated from the vacuum line, was exposed to the heated precursor (65°C) with a flow of 0.5 sccm N_2 , resulting in a pressure increase rate of ~ 40 mtorr/s. Standard flow conditions were used for air and N_2 pulses. As the focus of this work is on the ultra-low loading regime, the CAs were exposed to 2, 5, and 10 ALD cycles.

After ALD coating, the distributions and morphologies of Pt nanoparticles in CAs were characterized with Rutherford backscattering spectrometry (RBS, with 2 MeV ^4He ions backscattered to 164°) and cross-sectional transmission electron microscopy (XTEM, Philips CM-300 FEG). A focused ion beam instrument was used to prepare XTEM cross-sections. To extract the depth profiles of the Pt atomic concentration from RBS spectra, we used the RUMP code¹⁷ as described elsewhere.¹¹ Oxidation of carbon monoxide, a well studied model reaction, was used to characterize the catalytic activity of the resulting structures.¹⁸ The specific surface area (SSA) was estimated based on Brunauer-Emmett-Teller (BET) N_2 adsorption method.

Our structural characterization reveals that ALD is an efficient method to deposit highly dispersed Pt nanoparticles on the inner surfaces of CA monoliths. Figure 1(a) shows a low-magnification XTEM image of a CA treated with 10 ALD cycles, illustrating the expected sponge-like structure of the macroporous CA support. Figures 1(b), (c), and (d) are higher magnification XTEM images of the Pt-CA composite taken at depths of ~ 1 , 5 , and $10\ \mu\text{m}$ below

the surface, respectively. These images clearly show the formation of discrete Pt nanoparticles on the interior surface of the CA. The crystallinity of the Pt nanoparticles is confirmed by a high-resolution XTEM image shown in Figure 1(e) as well as by our selected area diffraction pattern analysis [Fig. 1(e), inset].

Further analysis of XTEM images [Fig. 1(f)] reveals that the average particle size decreases with increasing depth, from ~ 4.2 nm at the CA monolith surface to ~ 2.4 nm at a depth of 5 μm . Between 5 μm and 10 μm , the average particle size remains nearly constant (~ 2.3 nm), whereas the density of Pt nanoparticles slightly decreases (see below). Figure 1(e) also reveals the relatively narrow size distribution of the deposited Pt nanoparticles for all three depths studied (standard deviations of ~ 1.4 , 0.8, and 0.6 nm for 1, 5, and 10 μm below the surface, respectively). The depth dependence of Pt particle sizes revealed by Fig. 1 indicates a non-ideal ALD process. As discussed in detail elsewhere,¹¹ a non-ideal ALD behavior, such as revealed by Fig. 1, could be attributed to precursor reactivity and to processes of adsorption-desorption equilibrium of both precursor and reaction product molecules with pore walls. Although we only characterized the 10 cycle Pt-CA sample by XTEM, very similar results - except for the lower coverage - can be expected for the 2 and 5 cycle samples.

Our attempts to determine the Pt loading using CO adsorption measurements were unsuccessful since the Pt amount was below the detection limits ($\sim 10^{-6}$ mol). Instead, RBS was used to quantify the near-surface sample composition (up to ~ 6 microns from the surface). Depth profiles of the Pt concentration in CAs are shown in Figure 2, indicating that the concentration of Pt increases with increasing the number of ALD cycles. In addition, for all three cases (of 2, 5, and 10 cycles), a higher Pt concentration is observed at the monolith surface, which is in agreement with XTEM data. Surface concentrations of 8.3, 2.3, and 1.5 Pt at.% were observed

for the 10, 5, and 2 cycle Pt-CA, respectively. Concentrations of 2.0, 0.4, and 0.4 Pt at,% were observed at a depth of 6 μm for the 10, 5, and 2 cycle Pt-CA. The greater difference between 5 and 10 cycle Pt-CA is attributed to the existence of an ALD incubation period and a resulting lower growth rate that is often observed during the first several cycles of Pt ALD.¹⁵ Results from Fig. 2 suggest extremely low Pt loadings (i.e., the total weight of Pt atoms per area of the CA disk) of 0.26, 0.066, and 0.047 mg/cm^2 for the 10, 5, and 2 cycle Pt-CA. Our results also show that the SSA of Pt-CA composites slightly increases with the number of ALD cycles. The SSA values are 454, 593, and 626 m^2/g for the 2, 5, and 10 cycle samples, respectively. In view of the low Pt loading levels revealed by RBS, this increase in surface area is likely due to O_2 activation of the CA structure during the dry air portion of the ALD cycle.

Despite their very low loading levels, the Pt-CA composite materials were found to be highly active as catalysts for CO oxidization. The catalytic activity of these materials was characterized in a continuous flow reactor constructed of glass tubing (see the inset in Figure 3(b)). The reactor was equipped with a glass frit in the lower section for supporting monolithic parts of the Pt-CA composites.¹⁹ Gases were pre-heated by flowing them through a helical glass coil encircled reactor (30 cm height, 2 cm inner diameter) housed in a tube furnace. Dry synthetic air (80/20 vol% N_2/O_2) and CO were injected into the apparatus with a total gas flow of 50 sccm (mass flow controllers, Maettig Bronkhorst). The amount of CO_2 at the reactor outlet was monitored with an infrared-gas-analyzer (IRGA, “URAS 3G”, Hartmann und Braun). All samples were cleaned by heating to above 200 $^\circ\text{C}$ for several minutes before the measurements were started. Afterwards, nearly full conversion of CO to CO_2 was observed even when temperatures were reduced to 150 $^\circ\text{C}$, whereas, no conversion of CO was observed for undoped CA samples. Figure

3(a) shows a typical data set collected at 250°C. The CO₂ concentration measured at the reactor outlet follows the CO concentration as the latter is increased in a stepwise fashion.

The most surprising result is that the activity of our 2 ALD cycle Pt-CA samples was as high as that of the 10 ALD cycle samples. Figure 3(b) shows conversion rates per gram as the ratio of CO and O₂ was increased. For this experiment, the reactor temperature was held at 250 °C, and data was acquired for the 2, 5, and 10 cycle Pt-CA. Using the measured composition of the outlet gas, a conversion rate was calculated, which was then divided by the measured sample mass to yield a conversion rate per gram. Most significantly, the observed conversion rate dependence was found to be sample independent (i.e. the catalytic activity of the sample prepared with two ALD cycles was just as high as that of the sample prepared with ten cycles), indicating that, for the conditions used, the samples contained an excess of reactive Pt sites. Indeed, we observed that the conversion rate is limited by the thermal stability of our Pt-CA composite material which starts to degrade at a power production of 160 W/g. Furthermore, the linear relationship between conversion rate and the CO/O₂ ratio shown in Figure 3(b) reveals that the conversion efficiency is near 100%.(footnote 19)

To quantify the reaction kinetics, the turnover frequency (TOF) of the Pt-CA catalyst was estimated based on TEM and RBS results. Our analysis is based on the assumptions that (1) the particles have a hemispherical shape and that (2) every surface atom is catalytically active, i.e. an active site. For the two cycle sample this leads to a TOF between 4 s⁻¹ and 29 s⁻¹ depending on the assumptions made regarding mass transport limitations, that is, full penetration of reactants throughout the cross-section of the Pt-CA versus considering only the outer 10 μm of the material. The latter case appears more reasonable due to the rapid consumption of reactants, independent of the total Pt loading. In any case, the numbers are in good agreement with model

experiments.¹⁸ However, the extent of mass transport limitation could not be determined quantitatively on the basis of the present experiments but will be addressed in future studies.

In summary, we have successfully demonstrated the fabrication of catalytically-active Pt-loaded CA materials using ALD. Structural analysis of these materials confirmed the growth of discrete crystalline Pt nanoparticles to a depth of a few microns within the CA support. Beside some non-ideal ALD process close to the surface the particle size was below 5 nm. RBS analysis showed that the Pt loading in the CAs is extremely low, with the areal density of Pt estimated to be $\sim 0.047 \text{ mg/cm}^2$ in the sample prepared with 2 ALD cycles. Remarkably, even at such low loading levels, these materials exhibited high catalytic activity. Carbon monoxide oxidation studies demonstrated near 100% conversion of CO to CO₂ at temperatures ranging from 150 °C to 250 °C, with stability up to a power production of 160 Wg^{-1} ($6 \cdot 10^{-4} \text{ mol g}^{-1}\text{s}^{-1}$ at 250 °C). In case of the 2 ALD cycle Pt-CA sample, the turnover frequency lies in the range of $4\text{-}29 \text{ s}^{-1}$ depending on the assumptions made on mass transport. The technique demonstrated here can be applied to the design of new catalytic materials for a variety of applications, including fuel cells, hydrogen storage, pollution control, green chemistry, and liquid fuel production.

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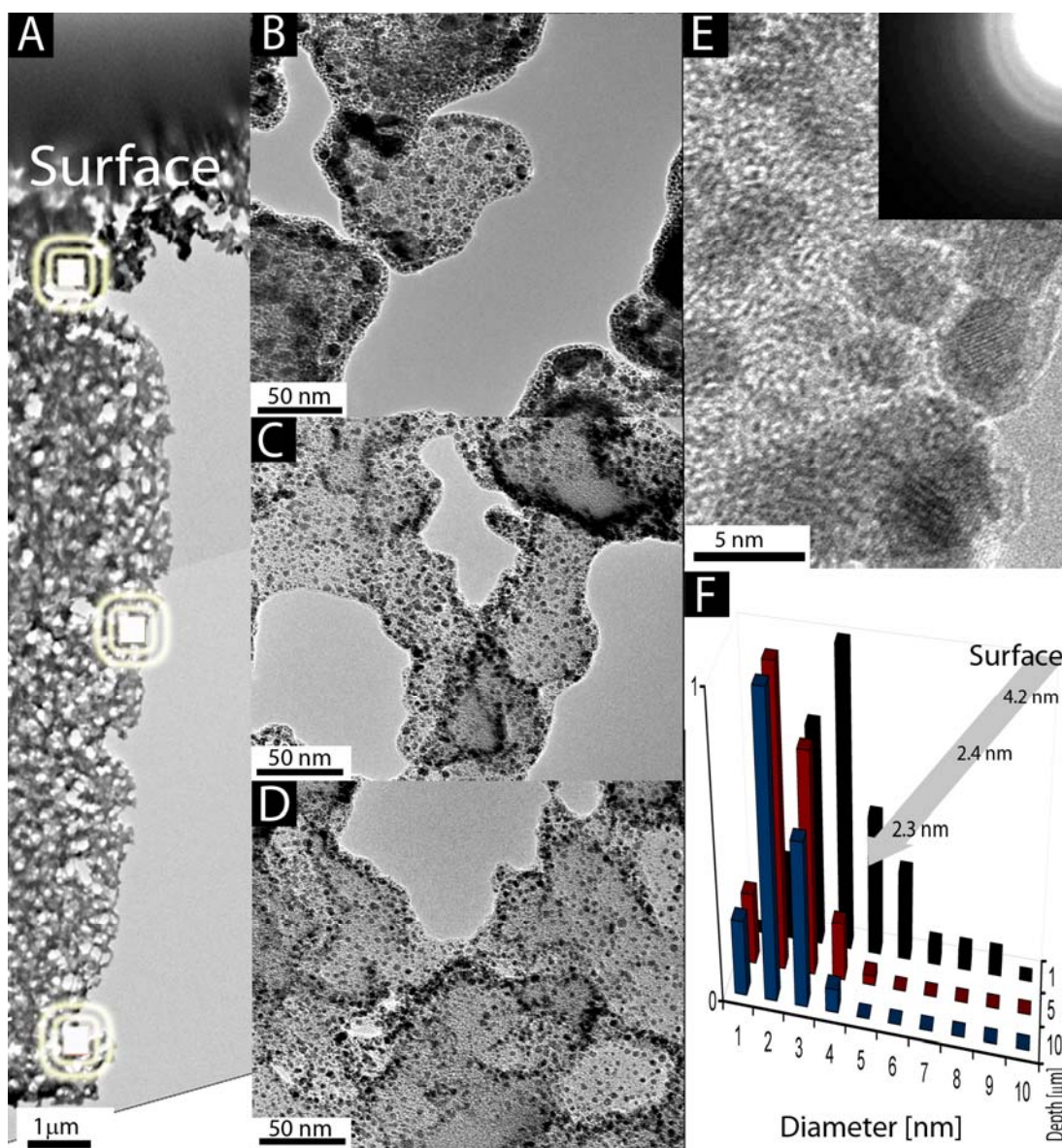


Figure 1. XTEM micrographs of a carbon aerogel treated with 10 Pt ALD cycles. (a) Low magnification image. Higher magnification images taken from sample regions marked in (a) and corresponding to depth of (b) 1 μm , (c) 5 μm , and (d) 10 μm below the monolith surface, with particle size histograms and resulting average particle diameter shown in (f). (e) High resolution image, and a selected-area diffraction pattern in the inset, indicating crystallinity of the ALD-deposited Pt nanoparticles at a depth of $\sim 1 \mu\text{m}$ from the sample surface.

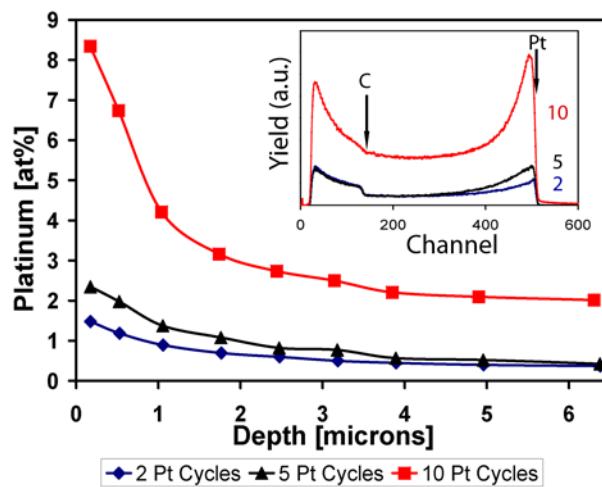


Figure 2. Depth profiles of the Pt concentration in a carbon aerogel infiltrated with 2, 5, and 10 Pt ALD cycles (as indicated in the legend) calculated from RBS spectra shown in the inset.

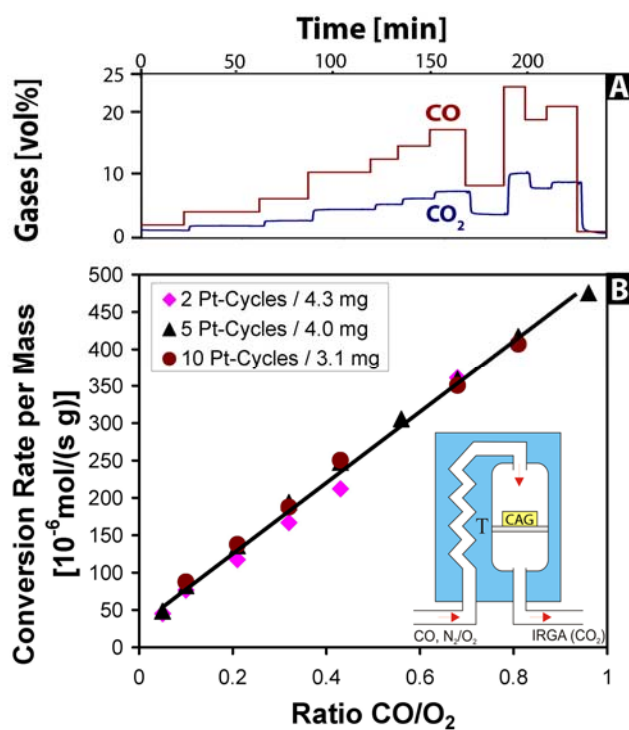


Figure 3. CO oxidation data for Pt-CA nanocomposites. (a) Time series of CO (inlet) and the resulting CO₂ signal at the reactor outlet for 4.0 mg of the 10 ALD cycle Pt-CA. (b) Conversion rate dependence of 2, 5, and 10 ALD cycle Pt-CA on the ratio of CO to O₂ (concentrations at the inlet).

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19. It should be noted that the sample did not fill the area of the frit, thus a portion of the gas stream by-passed the sample; this was the case especially during measurements where smaller amounts of catalyst were used.